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Effect of nature and extent of functional group modification on properties of thermosets from methacrylated epoxidized sucrose soyate

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ABSTRACT

A study was carried out to evaluate the impact of modification of epoxidized sucrose soyate using a combination of methacrylate and inert esters (acetate propionate, butyrate) on the properties of the resins as well as the thermosets. Previous studies have shown that methacrylated epoxidized sucrose soyate (MESS) can yield thermosets having high glass transition temperature (T_g) and good mechanical properties, but had high resin viscosity due to hydrogen bonding of the hydroxyl groups. Further functionalization to yield dimethacrylated epoxidized sucrose soyate (DMESS) resulted in reduced resin viscosity, but some of the thermosets were brittle. In this study, to maintain low resin viscosity and improve thermoset ductility, replacement of some methacrylate groups with various ester groups was explored. The synthesis of these resins was carried out in a one-pot process involving the sequential slow addition of anhydrides of the acids mixed prior to addition. The synthesized resins were characterized for their viscosity with and without styrene diluent. Formulations were made using varying amounts of styrene and free-radically cured using peroxyesters as initiators. The bio-based resins with 30% styrene gave much lower viscosities compared to commercial resins containing higher amounts of styrene (33% and 45%). The thermosets produced had improved flexibility and toughness with only a slight reduction in the glass transition temperature. The inclusion of the non-functional esters in the resin structure acted as internal plasticizers for the polymer system. The new sets of thermomechanical properties demonstrated the tunability of the bio-based resin system and opens up different avenues for end-use applications.

1. Introduction

Fluctuating costs and environmental concerns of petrochemicals have remained a main motivator of sustainability in polymer science. Vegetable oils have been sought as a chemical commodity to replace petrochemical sources due to their competitive cost, ready availability, built-in functionality, and numerous applications [1–6]. These oils are esters formed by glycerol and various fatty acids containing 8–24 carbon atoms and ranging from saturated to unsaturated types, depending on the plant type and source [7,8]. Polymerization of unmodified vegetable oils is typically done via autoxidation through the fatty acid double bonds [9]. However, these crosslinking processes require prolonged periods of time to fully cure. Due to this, modification of vegetable oils has been extensively explored. One of the more common modifications utilized has been the epoxidation of these oils. This epoxidation has become one of the routes used in creating materials possessing tunable properties.

SEFOSE 1618U (sucrose soyate) is a sucrose ester of fatty acid from soybean oil, which was commercialized by Procter and Gamble (P&G) Chemicals as a reactive diluent for alkyds [10–12]. It has a rigid sucrose core and flexible fatty acid side chains. Webster et al. epoxidized the sucrose soyate and optimized the process suitable for large-scale production [13–15]. Epoxidized sucrose soyate (ESS) contains about 12 epoxy groups per molecule and has shown promise in a wide range of crosslinking technologies [16]. This molecule has shown versatility in bio-based coatings applications such as polyurethanes [17], UV-curable [18], melamine-formaldehyde [19], acid-blocked [20], degradable [21,22], and high performance coatings [23,24]. Recently, ESS was shown to perform exceptionally well in terms of its adhesive property in fiberboards when used with a suitable crosslinker and catalyst [25]. Fiber reinforced polymer (FRP) composites have been developed using bio-based thermosets as the polymer matrix [26–33]. ESS has also shown promise in this application. High performance epoxy-anhydride thermosets for structural composites using ESS have shown high glass transition temperatures and Young's modulus [23]. Yan and Webster also studied novel bio-based methacrylated oligomers from ESS [34]. The thermosets produced from this resin gave improved thermomechanical properties that afforded them as FRP composite resin

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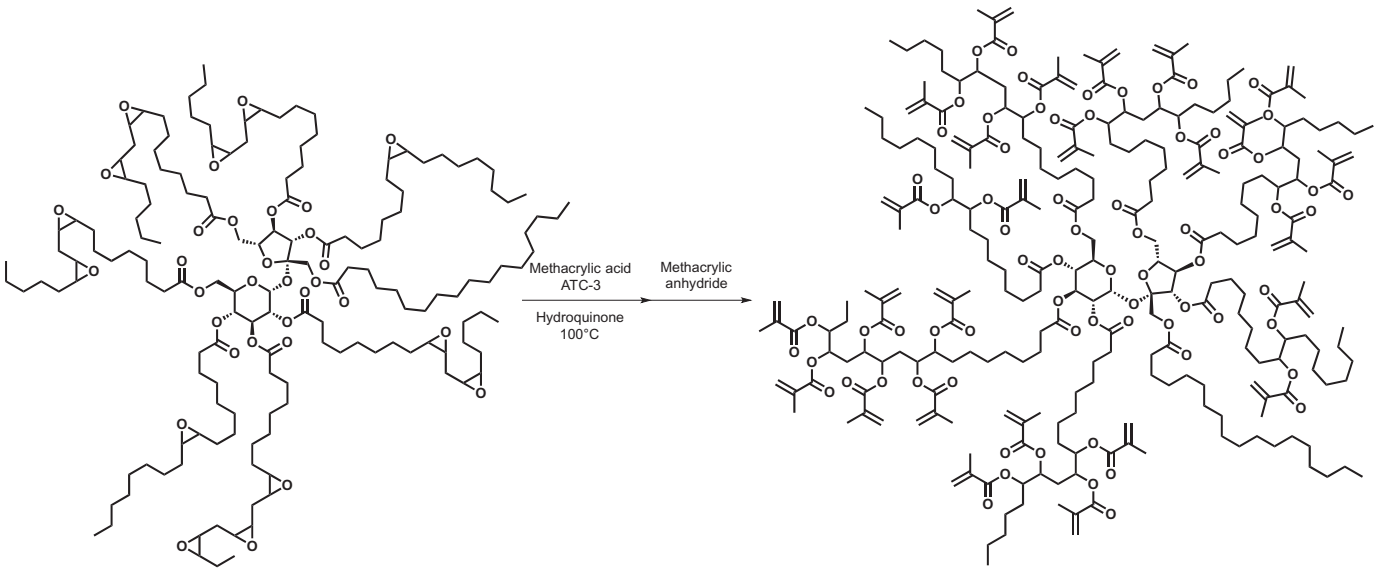
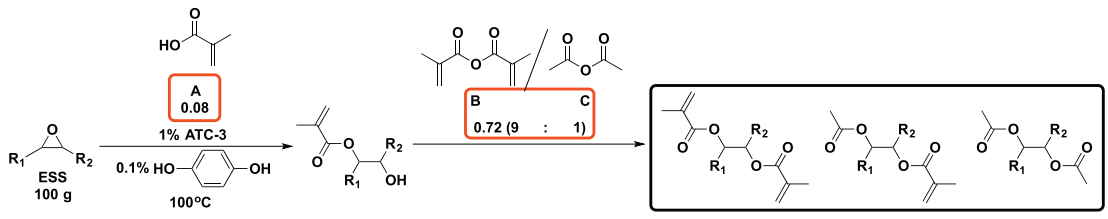
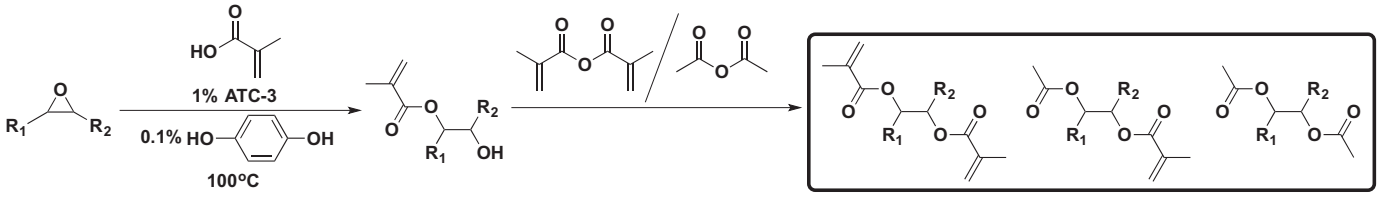


Scheme 1. Synthetic route to dimethacrylated epoxidized sucrose soyate (DMESS).

Table 1
Reagents used for the synthesis of the MASS, MPSS, and MBSS.



Resin	Second anhydride	B:C	Methacrylic anhydride (g) [B]	Second anhydride (g) [C]
MASS-0.1	Acetic anhydride	9:1	40.94	3.01
MASS-0.3	Acetic anhydride	7:3	31.84	9.04
MPSS-0.1	Propionic anhydride	9:1	40.94	3.84
MPSS-0.3	Propionic anhydride	7:3	31.84	11.52
MBSS-0.1	Butyric anhydride	9:1	40.94	4.67
MBSS-0.3	Butyric anhydride	7:3	31.84	14.00



Scheme 2. Synthesis of MASS.

matrix [35].

Plasticizers are typically used as additives in polymer industries. These are relatively low molecular weight non-volatile compounds that soften materials [36]. Plasticizers alter the physical properties of a polymer by increasing the free volume of the overall polymer network. Consequently, the glass transition temperature is lowered while the flexibility, elongation, and toughness is increased. They also lower resin viscosity by increasing the mobility of the polymer chains making the material more processible [37]. Generally, plasticizers are classified as either external or internal. External plasticizers are not physically bound and may exude from the polymer while internal plasticizers are chemically bound within the polymer chain. The effects of external bio-based plasticizers such as epoxidized soybean oil (ESO) on thermomechanical properties of polymers have been studied [38–40]. Similarly, the effects of bound dangling chains on the thermo-mechanical properties of polymer have also been proven to function as immobile internal plasticizers [41,42]. A recent review by Vieira et al. [43] discussed the current developments on natural-based plasticizers in the last decade.

In conjunction with flax and glass fibers, MESS has been investigated and has shown interesting sets of properties that displayed complex behavior [44–46]. When used with glass fibers, MESS had better adhesion to the fibers than a conventional vinyl ester resin [35]. Despite the improved thermomechanical properties of MESS, its resin viscosity was high due to the hydrogen bonding of the secondary hydroxyl group generated from the epoxide ring-opening reaction. The